Congener-Specific Numbering Systems for the Environmentally Relevant C_4 through C_8 Perfluorinated Homologue Groups of Alkyl Sulfonates, Carboxylates, Telomer Alcohols and Acids and Their Derivatives

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Introduction

We introduce a congener-specific numbering system for the C_4 through C_8 perfluorinated homologue groups of alkyl sulfonates, carboxylates, telomer alcohols and acids, and their derivatives. Increasing length of the carbon chain beyond C_3 leads to a corresponding rapid increase in the number of potential isomers (C_4=4, C_5=8, C_6=17, C_7=39, and C_8=89 congeners). There is a need for clear and unambiguous chemical shorthand to ensure accuracy and consistency in the future perfluorinated alkyl substance (PFA) literature, and to correct previous misconceptions that may have restricted research efforts into developing full-congener PFA analysis. If adopted by the research community, introduction of a numbering system at this relatively early stage of investigations into the congener-specific analysis, environmental behavior, and toxicology of PFAs would not require an arduous and difficult reassignment of historical structures and naming conventions presented in the prior art. Many PFA congeners are chiral (chiral centers denoted by a "*" in Figures 2 through 6), necessitating a consideration of their enantiospecific environmental behavior and toxicology.

Table 1. *Number of PFA congeners and stereoisomers in each of the C_3 through C_8 homologues.*

Homologue group	# of congeners	# of chiral congeners	# with 1 chiral center	# with 2 chiral centers	# with 3 chiral centers	Total number of stereoisomers
3	2	0	-	-	-	-
4	4	1	1	-	-	2
5	8	3	3	-	-	6
6	17	9	8	1	-	20
7	39	24	19	5	-	58
8	89	66	48	17	1	172

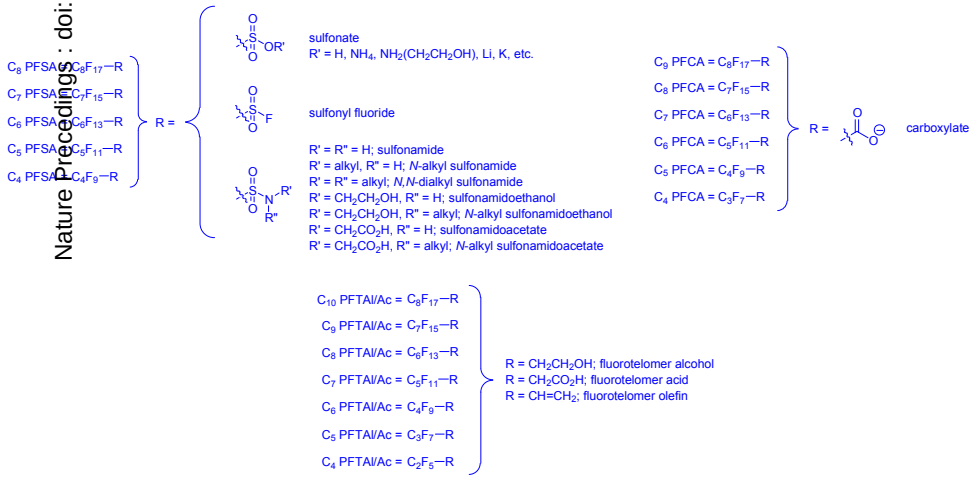


Figure 1. *PFA structures for which the proposed numbering system applies.*

Figure 2. *Structures and numbering system for the C_4 perfluorinated chains.*

	#	Substitution	Structure
C_4	1	1,1'-dimethylethyl	
	2	1-methylpropyl	
	3	2-methylpropyl	
	4	n-butyl	

Figure 3. *Structures and numbering system for the C_5 perfluorinated chains.*

	#	Substitution	Structure
C_5	1	1-ethylpropyl	
	2	1,1'-dimethylpropyl	
	3	1,2-dimethylpropyl	
	4	2,2'-dimethylpropyl	
	5	1-methylbutyl	
	6	2-methylbutyl	
	7	3-methylbutyl	
	8	n-pentyl	

Figure 4. *Structures and numbering system for the C_6 perfluorinated chains.*

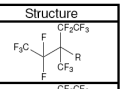
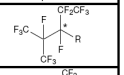
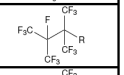
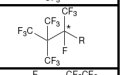
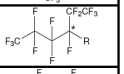
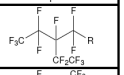
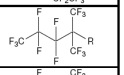
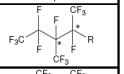
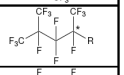
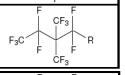
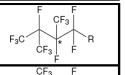
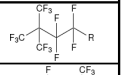
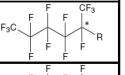
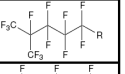
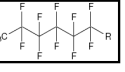
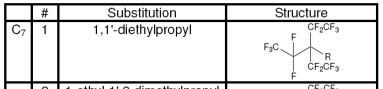
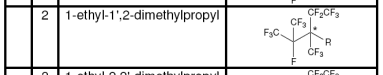
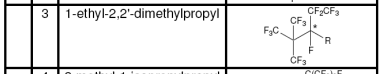
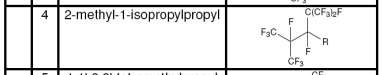
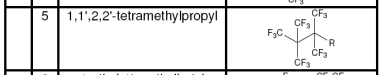
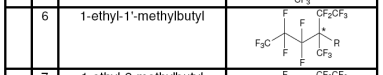
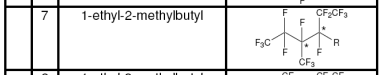
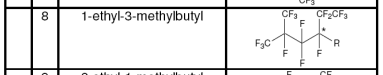
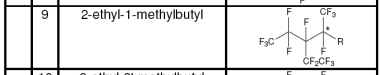
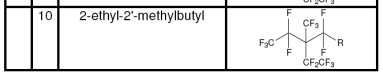
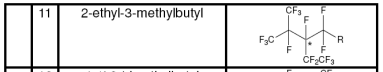
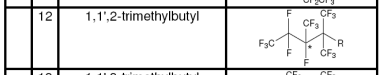
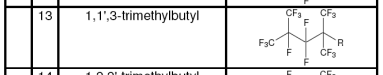
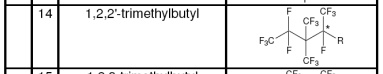
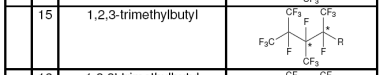
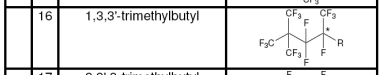
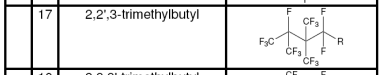
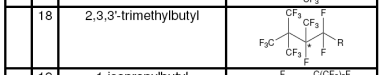
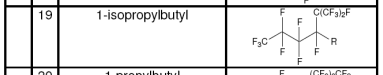
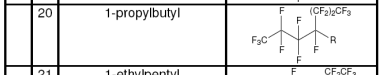
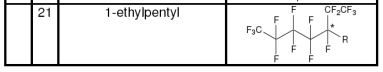
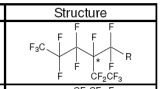
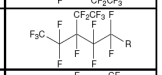
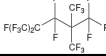
	#	Substitution	Structure
C_6	1	1-ethyl-1-methylpropyl	
	2	1-ethyl-2-methylpropyl	
	3	1,1',2-trimethylpropyl	
	4	1,2,2'-trimethylpropyl	
	5	1-ethylbutyl	
	6	2-ethylbutyl	
	7	1,1'-dimethylbutyl	
	8	1,2-dimethylbutyl	
	9	1,3-dimethylbutyl	
	10	2,2'-dimethylbutyl	
	11	2,3-dimethylbutyl	
	12	3,3'-dimethylbutyl	
	13	1-methylpentyl	
	14	2-methylpentyl	
	15	3-methylpentyl	
	16	4-methylpentyl	
	17	n-hexyl	

Figure 5. *Structures and numbering system for the C_7 perfluorinated chains.*

	#	Substitution	Structure
C_7	1	1,1'-diethylpropyl	
	2	1-ethyl-1',2-dimethylpropyl	
	3	1-ethyl-2,2'-dimethylpropyl	
	4	2-methyl-1-isopropylpropyl	
	5	1,1',2,2'-tetramethylpropyl	
	6	1-ethyl-1'-methylbutyl	
	7	1-ethyl-2-methylbutyl	
	8	1-ethyl-3-methylbutyl	
	9	2-ethyl-1-methylbutyl	
	10	2-ethyl-2'-methylbutyl	
	11	2-ethyl-3-methylbutyl	
	12	1,1',2-trimethylbutyl	
	13	1,1',3-trimethylbutyl	
	14	1,2,2'-trimethylbutyl	
	15	1,2,3-trimethylbutyl	
	16	1,3,3'-trimethylbutyl	
	17	2,2',3-trimethylbutyl	
	18	2,3,3'-trimethylbutyl	
	19	1-isopropylbutyl	
	20	1-propylbutyl	
	21	1-ethylpentyl	

	#	Substitution	Structure
C_7	22	2-ethylpentyl	
	23	3-ethylpentyl	
	24	1,1'-dimethylpentyl	
	25	1,2-dimethylpentyl	
	26	1,3-dimethylpentyl	
	27	1,4-dimethylpentyl	
	28	2,2'-dimethylpentyl	
	29	2,3-dimethylpentyl	
	30	2,4-dimethylpentyl	
	31	3,3'-dimethylpentyl	
	32	3,4-dimethylpentyl	
	33	4,4'-dimethylpentyl	
	34	1-methylhexyl	
	35	2-methylhexyl	
	36	3-methylhexyl	
	37	4-methylhexyl	
	38	5-methylhexyl	
	39	n-heptyl	

	#	Substitution	Structure
C_8	1	1-ethyl-1',2,2'-trimethylpropyl	
	2	1-ethyl-1'-isopropylpropyl	
	3	1-isopropyl-1',2-dimethylpropyl	
	4	1-isopropyl-2,2'-dimethylpropyl	
	5	1-*tert*-butyl-butyl	
	6	1,1'-diethylbutyl	
	7	1,2-diethylbutyl	
	8	2,2'-diethylbutyl	
	9	1-*iso*propyl-1'-methyl-butyl	
	10	1-*iso*propyl-2-methylbutyl	
	11	1-*iso*propyl-3-methylbutyl	
	12	2-*iso*propyl-3-methylbutyl	
	13	1-ethyl-1',2-dimethylbutyl	
	14	1-ethyl-1,3-dimethylbutyl	
	15	1-ethyl-2,2'-dimethylbutyl	
	16	1-ethyl-2,3-dimethylbutyl	
	17	1-ethyl-3,3'-dimethylbutyl	
	18	2-ethyl-1,1'-dimethylbutyl	
	19	2-ethyl-1,2'-dimethylbutyl	
	20	2-ethyl-1,3-dimethylbutyl	
	21	2-ethyl-2',3-dimethyl-butyl	

	#	Substitution	Structure
C_8	22	2-ethyl-3,3'-dimethylbutyl	
	23	1,1',2,2'-tetramethylbutyl	
	24	1,1',2,3-tetramethylbutyl	
	25	1,1',3,3'-tetramethylbutyl	
	26	1,2,2',3-tetramethylbutyl	
	27	1,2,3,3'-tetramethylbutyl	
	28	2,2',3,3'-tetramethylbutyl	
	29	2,2',4,4'-tetramethylbutyl	
	30	1-propyl-1'-methylbutyl	
	31	1-propyl-2-methylbutyl	
	32	1-propyl-3-methylbutyl	
	33	1-ethyl-1'-methylpentyl	
	34	1-ethyl-2-methylpentyl	
	35	1-ethyl-3-methylpentyl	
	36	1-ethyl-4-methylpentyl	
	37	2-ethyl-1-methylpentyl	
	38	2-ethyl-2-methylpentyl	
	39	2-ethyl-3-methylpentyl	
	40	2-ethyl-4-methylpentyl	
	41	3-ethyl-1-methylpentyl	
	42	3-ethyl-2-methylpentyl	

	#	Substitution	Structure
C_8	43	3-ethyl-3'-methylpentyl	
	44	3-ethyl-4-methylpentyl	
	45	1-*iso*propylpentyl	
	46	2-*iso*propylpentyl	
	47	1,1',2-trimethylpentyl	
	48	1,1',3-trimethylpentyl	
	49	1,1',4-trimethylpentyl	
	50	1,2,2'-trimethylpentyl	
	51	1,2,3-trimethylpentyl	
	52	1,2,4-trimethylpentyl	
	53	1,3,3'-trimethylpentyl	
	54	1,3,4-trimethylpentyl	
	55	1,4,4'-trimethylpentyl	
	56	2,2',3-trimethylpentyl	
	57	2,3,3'-trimethylpentyl	
	58	2,3,4-trimethylpentyl	
	59	2,4,4'-trimethylpentyl	
	60	3,3',4-trimethylpentyl	
	61	3,4,4'-trimethylpentyl	
	62	1-propylpentyl	
	63	2-propylpentyl	

	#	Substitution	Structure
C_8	64	1-ethylhexyl	
	65	2-ethylhexyl	
	66	3-ethylhexyl	
	67	4-ethylhexyl	
	68	1,1'-dimethylhexyl	
	69	1,2-dimethylhexyl	
	70	1,3-dimethylhexyl	
	71	1,4-dimethylhexyl	
	72	1,5-dimethylhexyl	
	73	2,2'-dimethylhexyl	
	74	2,3-dimethylhexyl	
	75	2,4-dimethylhexyl	
	76	2,5-dimethylhexyl	
	77	3,3'-dimethylhexyl	
	78	3,4-dimethylhexyl	
	79	3,5-dimethylhexyl	
	80	4,4'-dimethylhexyl	
	81	4,5-dimethylhexyl	
	82	5,5'-dimethylhexyl	
	83	1-methylheptyl	
	84	2-methylheptyl	
	85	3-methylheptyl	
	86	4-methylheptyl	
	87	5-methylheptyl	
	88	6-methylheptyl	
	89	*n*-octyl	

Figure 6. *Structures and numbering system for the C_8 perfluorinated chains.*

Conclusion

The proposed numbering system for PFAs presented herein offers a concise and unambiguous means for communicating molecular structures of these important contaminants within the scientific literature. In addition, the system outlines the number and range of possible structures that may be present in environmental and biological systems, and for which more comprehensive congener-specific analysis and testing methods should be developed.

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